

1 **COLD-BOX BINDERS CONTAINING**
2 **AN EPOXY RESIN AND ESTER OF A FATTY ACID**
3

4 **Field of the Invention**

5 This invention relates to foundry binder systems, which cure in the presence of sulfur
6 dioxide and an oxidizing agent, comprising (a) an epoxy resin; (b) an ester of a fatty
7 acid; (c) an effective amount of a oxidizing agent, and (d) no ethylenically unsaturated
8 monomer or polymer. The foundry binder systems are used for making foundry mixes.
9 The foundry mixes are used to make foundry shapes (such as cores and molds) which
10 are used to make metal castings.

11
12 **Description of the Related Art**

13 In the foundry industry, one of the procedures used for making metal parts is "sand
14 casting". In sand casting, disposable molds and cores are fabricated with a mixture of
15 sand and an organic or inorganic binder. The foundry shapes are arranged in core/mold
16 assembly, which results in a cavity into which molten metal will be poured. After the
17 molten metal is poured into the assembly of molds and cores and cools, the metal part
18 formed by the process is removed from the assembly. The binder is needed so the
19 molds and cores will not disintegrate when they come into contact with the molten
20 metal.

21
22 Two of the prominent fabrication processes used in sand casting are the no-bake and the
23 cold-box processes. In the no-bake process, a liquid curing catalyst or co-reactant is
24 mixed with an aggregate and binder to form a foundry mix before shaping the mixture
25 in a pattern. The foundry mix is shaped by putting it into a pattern and allowing it to
26 cure until it is self-supporting and can be handled. In the cold-box process, a gaseous
27 curing catalyst or co-reactant is passed through a shaped mixture (usually in a corebox)
28 of the aggregate and binder to cure the mixture.

29
30 A cold-box process widely used in the foundry industry for making cores and molds is

1 the "SO₂ cured epoxy/acrylate system". In this process, a mixture of a hydroperoxide
2 (usually cumene hydroperoxide), an epoxy resin, a multifunctional acrylate, typically a
3 coupling agent, and optional diluents, are mixed into an aggregate (sand) and
4 compacted into a specific shape, typically a core or mold. Sulfur dioxide (SO₂),
5 optionally diluted with nitrogen or another inert gas, is blown into the binder/aggregate
6 shape. The shape is instantaneously hardened and can be used immediately in a
7 foundry core/mold system. In this binder system, the acrylate component must be kept
8 separate from the hydroperoxide until the binder is applied to sand, otherwise, free
9 radical polymerization of the acrylate component will begin prematurely and render the
10 binder useless.

11
12 German Patent Application DE 197 27 540 discloses examples of epoxy-acrylic
13 foundry binders containing methyl-, ethyl- and propyl-esters of oleic acid, which are
14 cured with sulfur dioxide in the presence of a free radical initiator.

15 16 **Brief Summary of the Invention**

17 The subject invention relates to foundry binder systems, which cure in the presence of
18 gaseous sulfur dioxide and an oxidizing agent, comprising:

- 19 (a) 45 to 80 parts by weight of an epoxy resin;
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21 (b) 5 to 40 of ester of a fatty acid;
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23 (c) an effective amount of an oxidizing agent; and
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25 (d) 0 parts of an ethylenically unsaturated monomer or polymer.

26
27 wherein (a), (b), and (c) are separate components or mixed with another of said
28 components, and where said parts by weight are based upon 100 parts of binder.

1 It has been found that addition of the ester of the fatty acid to this acrylate-free binder
2 provides foundry shapes that have better tensile strength development and humidity
3 resistance than cores and molds made with binders containing an ethylenically
4 unsaturated monomer or polymer. A cycloaliphatic epoxy resin is particularly preferred
5 when the interest is obtaining cores with improved humidity resistance. The
6 improvements in tensile strength development permits the foundry to use lower binder
7 levels in the core-making process. This is beneficial in the casting of both light metal
8 (e.g. aluminum) and ferrous parts.

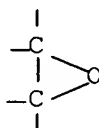
10 Another advantage of the binder, because it is acrylate-free, is that all of the
11 components of the binder can be sold and used in one package. This simplifies the
12 customer's binder storage and handling operations.

14 The foundry binders are used for making foundry mixes. The foundry mixes are used
15 to make foundry shapes, such as cores and molds, which are used to make metal
16 castings.

18 **Detailed Description of the Invention**

19 The detailed description and examples will illustrate specific embodiments of the
20 invention will enable one skilled in the art to practice the invention, including the best
21 mode. It is contemplated that many equivalent embodiments of the invention will be
22 operable besides these specifically disclosed. All percentages are percentages by
23 weight unless otherwise specified.

25 An epoxy resin is a resin having an epoxide group, i.e.,



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4 such that the epoxide functionality of the epoxy resin (epoxide groups per molecule) is
5 equal to or greater than 1.9, typically from 2.0 to 4.0.
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7 Examples of epoxy resins include (1) diglycidyl ethers of bisphenol A, B, F, G and H,
8 (2) halogen-substituted aliphatic epoxides and diglycidyl ethers of other bisphenol
9 compounds such as bisphenol A,B, F, G, and H, and (3) epoxy novolacs, which are
10 glycidyl ethers of phenolic-aldehyde novolacs, (4) cycloaliphatic epoxy resins, and (5)
11 mixtures thereof.
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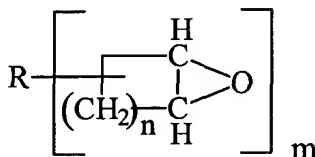
13 Epoxy resins (1) are made by reacting epichlorohydrin with the bisphenol compound in
14 the presence of an alkaline catalyst. By controlling the operating conditions and
15 varying the ratio of epichlorohydrin to bisphenol compound, products of different
16 molecular weight can be made. Epoxy resins of the type described above based on
17 various bisphenols are available from a wide variety of commercial sources.
18

19 Examples of epoxy resins (2) include halogen-substituted aliphatic epoxides, diglycidyl
20 ethers of other bisphenol compounds such as bisphenol A, B, F, G, and H, and epoxy
21 novolac resins. Examples of halogen-substituted aliphatic epoxides include
22 epichlorohydrin, 4-chloro-1, 2-epoxybutane, 5-bromo-1,2-epoxypentane, 6-chloro-1,3-
23 epoxyhexane and the like.
24

25 Examples of epoxy novolacs (3) include epoxy cresol and epoxy phenol novolacs,
26 which are produced by reacting a novolac resin (usually formed by the reaction of
27 orthocresol or phenol and formaldehyde) with epichlorohydrin, 4-chloro-1, 2-
28 epoxybutane, 5-bromo-1,2-epoxypentane, 6-chloro-1, 3-epoxyhexane and the like.
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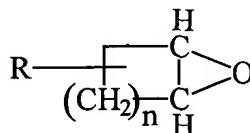
Examples of cycloaliphatic epoxy resins include any aliphatic, cycloaliphatic, or mixed aliphatic-cycloaliphatic epoxide having any aliphatic groups, and further includes aliphatic epoxy resins having aromatic groups, i.e. mixed aliphatic-aromatic epoxy resins. The aliphatic epoxy resin may contain monomeric epoxide compounds in admixture with polymeric epoxide compounds. The most preferred aliphatic epoxy resins are represented by the following structural formulae:

(I)



where "n" ≥ 1 and "m" is a whole number, typically from 1 to 4, preferably from 2-3, or

(II)



where "n" ≥ 1.

R in structures I and II is predominantly aliphatic in nature, but may contain oxygen functionality as well as mixed aliphatic-aromatic groups. Typically, R is selected from the group consisting of alkyl groups, cycloalkyl groups, mixed alkyl-cycloaliphatic groups, and substituted alkyl groups, cycloalkyl groups, or alkyl-cycloaliphatic groups, where the substituents include, for example, ether, carbonyl, and carboxyl groups.

1 Specific examples of aliphatic epoxy resins include 3,4-epoxycyclohexylmethyl-3,4-
2 epoxycyclohexane carboxylate; vinylcyclohexene dioxide; 2-(3,4-epoxycyclohexyl-5,5-
3 spiro-3,4-epoxy) cyclohexane-meta-dioxane; bis-(3,4-epoxycyclohexyl) adipate; 1,2-
4 epoxy-p-vinylcyclohexene; limonene dioxide; limonene monoxide; and hydrogenated
5 bisphenol diglycidyl ethers.

6
7 Preferably used are epoxy resins having an average epoxide functionality of at least 2.1
8 to 3.5, preferably from about 2.3 to about 3.0. Particularly preferred are epoxy resins
9 having an average weight per epoxy group of 165 to 200 grams/equivalent.

10
11 Although it is contemplated that any esters of a fatty acid can be used in this invention,
12 preferably used are esters of fatty acids where the fatty acid used to prepare the ester has
13 a carbon chain of 12 carbon atoms or more, particularly 12 to 22 carbon atoms.
14 Preferably the ester group of the ester of the fatty acid has 1 to 8 carbon atoms, most
15 preferably 1 to 4 carbon atoms. The esters of the fatty acids can be readily prepared by
16 transesterification of fats and oils of plant or animal origin, which are normally
17 available in the form of triglycerides or can be prepared by esterification of fatty acids
18 obtained from such fats and oils.

19
20 Rapeseed oil methyl ester is a typical example of an ester derived from plant oil; it is a
21 suitable solvent, particularly since it is available at low cost in the form of diesel fuel.
22 But the esters of other plant oils, such as soybean oil, linseed oil, sunflower oil, peanut
23 oil, tung oil, palm kernel oil, coconut oil, castor oil and/or olive oil, can also be used. In
24 addition, marine animal oil, tallow oil, and animal fats can also serve as starting
25 materials for alkyl esters that are to be used according to this invention.

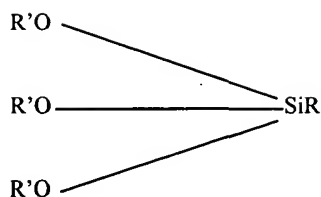
26
27 Particularly preferred are C₁-C₈ alkyl esters of fatty acid; e.g., methyl esters of rapeseed
28 oil, butyl tallate, and isooctyl tallate.

1 The oxidizing agent is a peroxide and/or hydroperoxide. Examples include ketone
2 peroxides, peroxy ester free radical initiators, alkyl oxides, chlorates, perchlorates, and
3 perbenzoates. Preferably, however, the free radical initiator is a hydroperoxide or a
4 mixture of peroxide and hydroperoxide. Hydroperoxides particularly preferred in the
5 invention include t-butyl hydroperoxide, cumene hydroperoxide, paramenthane
6 hydroperoxide, etc. The organic peroxides may be aromatic, aliphatic, or mixed
7 aromatic-aliphatic peroxides.

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9 Examples of useful diacyl peroxides include benzoyl peroxide, lauroyl peroxide and
10 decanoyl peroxide. Examples of mixed aromatic-aliphatic and aliphatic peroxides
11 respectively include dicumyl peroxide and di-t-butyl peroxide.

12
13 Solvents may also be added to the binder formulation. Typically, a solvent is used to
14 reduce the viscosity of the binder, such that the resulting viscosity of the epoxy resin
15 component is less than 1,000 centipoise, preferably less than 400 centipoise. Generally,
16 the total amount of solvent is used in an amount of 0 to 25 weight percent based upon
17 the total weight of the epoxy resin. Solvents that can be used include polar solvents,
18 such as liquid dialkyl esters, e.g. dialkyl phthalate of the type disclosed in U.S. Patent
19 3,905,934, and other dialkyl esters such as dimethyl glutarate, dimethyl succinate,
20 dimethyl adipate, and mixtures thereof. Suitable aromatic solvents are benzene, toluene,
21 xylene, ethylbenzene, and mixtures thereof. Preferred aromatic solvents are mixed
22 solvents that have an aromatic content of at least 90% and a boiling point range of
23 138°C to 232°C. Suitable aliphatic solvents include kerosene.

24
25 The binder may also contain a silane coupling agent having the following general
26 formula:



wherein R' is a hydrocarbon radical and preferably an alkyl radical of 1 to 6 carbon atoms and R is an alkyl radical, an alkoxy-substituted alkyl radical, or an alkyl-amine-substituted alkyl radical in which the alkyl groups have from 1 to 6 carbon atoms. The silane is preferably added to the binder in amounts of 0.01 to 2 weight percent, preferably 0.1 to 1.0 weight percent based on the weight of the binder.

Polyols such as phenolic resins, polyester resins, amine polyols, polyester polyols, and polyether polyols can also be used in the foundry binder.

Examples of phenolic resins include phenolic resole resins, particularly benzylic ether phenolic resole resins, including alkoxy-modified benzylic ether phenolic resole resins. Benzylic ether phenolic resole resins, or alkoxyated versions thereof, are well known in the art, and are specifically described in U.S. Patent 3,485,797 and 4,546,124.

Polyether polyols are prepared by reacting an alkylene oxide with a polyhydric alcohol in the presence of an appropriate catalyst such as sodium methoxide according to methods well known in the art.

The polyester polyols may be aliphatic and/or aromatic polyester polyols. These polyols generally having a hydroxyl number from about 200 to 2,000, preferably from 400 to 1000.

It will be apparent to those skilled in the art that other additives such as silicones, release agents, defoamers, wetting agents, etc. can be added to the aggregate, or foundry

1 mix. The particular additives chosen will depend upon the specific purposes of the
2 formulator.

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4 The components of the binder can be combined as one component and added to the
5 foundry aggregate, or can be added separately or in various combinations.

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7 Typically, the amounts of the components used in the binder system are from 45 to 80
8 parts by weight of epoxy resin, preferably from 50 to 70 parts by weight; from 5 to 40
9 parts by weight of an ester of a fatty acid, preferably from 15 to 30 parts by weight; and
10 from 10 to 40 parts by weight of oxidizing agent, preferably from 12 to 30 parts by
11 weight, where said parts by weight are based upon 100 parts of the binder system.

12

13 Various types of aggregate and amounts of binder are used to prepare foundry mixes by
14 methods well known in the art. Ordinary shapes, shapes for precision casting, and
15 refractory shapes can be prepared by using the binder systems and proper aggregate.

16 The amount of binder and the type of aggregate used are known to those skilled in the
17 art. The preferred aggregate employed for preparing foundry mixes is sand wherein at
18 least about 70 weight percent, and preferably at least about 85 weight percent, of the
19 sand is silica. Other suitable aggregate materials for ordinary foundry shapes include
20 zircon, olivine, aluminosilicate, chromite sands, and the like.

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22 In ordinary sand type foundry applications, the amount of binder is generally no greater
23 than about 10% by weight and frequently within the range of about 0.5% to about 7%
24 by weight based upon the weight of the aggregate. Most often, the binder content for
25 ordinary sand foundry shapes ranges from about 0.6% to about 5% by weight based
26 upon the weight of the aggregate in ordinary sand-type foundry shapes.

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28 The foundry mix is molded into the desired shape by ramming, blowing, or other
29 known foundry core and mold making methods. The shape is then cured almost

1 instantaneously by the cold-box process, using vaporized sulfur dioxide as the curing
2 agent (most typically a blend of nitrogen, as a carrier, and sulfur dioxide containing
3 from 35 weight percent to 65 weight percent sulfur dioxide), described in U.S. Patent
4 4,526,219 and 4,518,723, which are hereby incorporated by reference. The shaped
5 article is preferably exposed to effective catalytic amounts of gaseous sulfur dioxide,
6 and, optionally, minor amounts of a carrier gas can be used. The exposure time of the
7 sand mix to the gas is typically from 0.5 to 10 seconds. The foundry shape is cured
8 after gassing with sulfur dioxide. Oven drying may be needed if the foundry shape is
9 coated with a refractory coating.

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11 The core and/or mold may be formed into an assembly. When making castings, the
12 assembly may be coated with a water-based refractory coating and passed through a
13 conventional or microwave oven to remove the water from the coating.

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ABBREVIATIONS

16 The abbreviations used in the examples are as follows:

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18 SCA silane coupling agent.

19

20 Bis-A Epoxy bisphenol-A epoxy resin, 1.9 functionality, having epoxy
21 equivalent weight of about 184-192 grams/equivalent,
22 and a viscosity of 13,000 cp.

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24 BT butyl ester of tall oil fatty acid, PLASTHALL 503 from
25 CP Hall.

26

27 CHP cumene hydroperoxide.

28

29 EPALLOY 5000 a cycloaliphatic epoxy resin, which is prepared by

hydrogenating bisphenol-A glycidyl ether, manufactured
by CVC Specialty Chemicals.

ERL-4221 a cyloaliphatic epoxy resin, 3,4-epoxycyclohexylmethyl
3,4-epoxy-cyclohexane- carboxylate, manufactured by
Union Carbide.

EXAMPLES

While the invention has been described with reference to a preferred embodiment, those skilled in the art will understand that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims. In this application, all units are in the metric system and all amounts and percentages are by weight, unless otherwise expressly indicated.

Testing Protocol

The various formulations given in the following examples were evaluated by preparing test cores whose tensile strengths were measured over various times. How well a binder system bonds the particles of an aggregate (e.g. sand) together is typically evaluated by using tensile strength measurements given in pounds per square inch (psi). Sufficient core strength is needed once the binder/sand mix is cured to prevent the core/mold from distorting or cracking during assembly operations. Tensile strength measurements are taken immediately (20 seconds after core box opens), 5-minutes, one-hour, 24-hours and 24 hours at 90% relative humidity according to the standard ASTM sand tensile

test. Cores made with binder systems that retain higher tensile strengths over time can better retain their dimensional accuracy and have less core breakage problems.

Comparison Example A
(Binder containing epoxy resin and no ester of a fatty acid)

A one-part, acrylate-free binder system was prepared with bis-A epoxy resin having the following composition:

Bis A Epoxy	74.75
CHP	25.00
SCA	0.25

A foundry mix was prepared by mixing 2000 grams of silica sand and 16.0 grams of this binder. The binder was mixed for 4 minutes using a Hobart sand mixer. The foundry mix was blown into a three-cavity tensile test specimen core box and gassed 1.0 seconds with a 60/40 SO₂/nitrogen mixture delivered by an MT Systems SO₂/nitrogen blending unit followed by a 10 second dry air purge. The tensile strengths measurements are set forth in Table I.

Example 1
(Binder containing epoxy resin and an ester of a fatty acid)

A one-part, acrylate-free binder system was prepared with Bis-A epoxy resin and an ester of a fatty acid (BT) containing the following components:

Bis A Epoxy	52.5
BT	27.0
CHP	20.0
SCA	0.5

A foundry mix was prepared by mixing 2000 grams of silica sand and 16.0 grams of this binder. The binder was mixed for 4 minutes using a Hobart sand mixer. The

foundry mix was blown into a three-cavity tensile test specimen core box and gassed 1.0 seconds with a 60/40 SO₂/nitrogen mixture delivered by an MT Systems SO₂/nitrogen blending unit followed by a 10 second dry air purge. The tensile strengths measurements are set forth in Table I.

Table I
(Test results related to tensile strengths of cores made with binders containing bisphenol A epoxy resin)

Example	BT (pbw)	Tensile strengths of cores (psi)				
		Imm (20 sec)	5-min	1-hr	24 hrs	24 hr @ 95% RH
A	0	38	84	140	141	101
1	27	84	151	190	174	107

The data in Table I indicate that the overall tensile strengths made with the binder containing BT are improved.

Comparison Example B
(Binder containing cycloaliphatic epoxy resin and no ester of a fatty acid)

A one-part, acrylate-free binder was prepared by mixing the following compounds:

ERL 4221	79.5
CHP	20.0
SCA	0.5

A foundry mix was prepared by mixing 2000 grams of silica sand and 16.0 grams of this binder. The binder was mixed for 4 minutes using a Hobart sand mixer. The foundry mix was blown into a three-cavity tensile test specimen core box and gassed

1.0 seconds with a 60/40 SO₂/nitrogen mixture delivered by an MT Systems SO₂/nitrogen blending unit followed by a 10 second dry air purge. The tensile strengths measurements are set forth in Table II.

Example 2
(Binder containing cycloaliphatic epoxy resins and BT)

A one-part, acrylate-free binder was prepared by mixing the following components.

ERL 4221	69.5
BT	15.0
CHP	15.0
SCA	0.5

This binder uses a high level of ERL 4221 and a low level of BT.

A foundry mix was prepared by mixing 2000 grams of silica sand, 16.0 grams to the binder. The mixture was mixed for 4 minutes using a Hobart sand mixer. The sand/resin mix was then blown into a three cavity tensile test specimen core box and gassed 1.0 seconds with a 60/40 SO₂/nitrogen mixture delivered by an MT Systems SO₂/nitrogen blending unit followed by a 10 second dry air purge. The tensile strengths measurements are set forth in Table II.

Example 3
(Duplication of Example 2 using higher level of butyl tallate)

A one-part, acrylate-free binder was prepared by mixing the following components.

ERL 4221	57.5
BT	27.0
CHP	15.0
SCA	0.5

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This binder uses a lower level of ERL 4221 and a higher level of butyl tallate.

A foundry mixed was prepared by mixing 2000 grams of silica sand and 16.0 grams of the binder. The binder was mixed for 4 minutes using a Hobart sand mixer. The sand/resin mix was then blown into a three cavity tensile test specimen core box and gassed 1.0 seconds with a 60/40 SO₂/nitrogen mixture delivered by an MT Systems SO₂/nitrogen blending unit followed by a 10 second dry air purge. The tensile strengths measurements are set forth in Table II.

Example 4
(Binder containing mixture of cycloaliphatic epoxy resins and BT)

A one-part, acrylate-free binder system was prepared containing the following components:

ERL 4221	47.5
BT	22.0
CHP	15.0
Epalloy 5000	15.0
SCA	0.5

This binder uses a lower level of ERL 4221. A foundry mix was prepared by mixing 2000 grams of silica sand and 16.0 grams of binder. The foundry mix was mixed for 4 minutes using a Hobart sand mixer. The foundry mix was then blown into a three cavity tensile test specimen core box and gassed 1.0 seconds with a 60/40 SO₂/nitrogen mixture delivered by an MT Systems SO₂/nitrogen blending unit followed by a 10 second dry air purge. The tensile strengths measurements are set forth in Table II.

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Table II

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**(Test results related to tensile strengths of cores made with binders containing
cycloaliphatic epoxy resin)**

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		Tensile strengths of cores (psi)				
Example	BT (pbw)	Imm (20 sec)	5-min	1-hr	24 hrs	24 hr @ 95% RH
B	0	148	189	189	155	59
2	15	93	165	216	204	89
3	22	138	196	214	237	117
4	27	118	186	213	249	127

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6 The data indicate that by using increased levels of BT in binders containing a
7 cycloaliphatic epoxy resin it is possible to significantly improve the humidity resistance
8 of the cores made with the binder. This is particularly significant in foundries located
9 in warm, humid climates.

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